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Bandgap opening in hydrogenated germanene

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(Received 23 February 2018; accepted 16 April 2018; published online 26 April 2018)

We have studied the hydrogenation of germanene synthesized on Ge₂Pt crystals using scanning tunneling microscopy and spectroscopy. The germanene honeycomb lattice is buckled and consists of two hexagonal sub-lattices that are slightly displaced with respect to each other. The hydrogen atoms adsorb exclusively on the Ge atoms of the upward buckled hexagonal sub-lattice. At a hydrogen exposure of about 100 L, the (1 × 1) buckled honeycomb structure of germanene converts to a (2 × 2) structure. Scanning tunneling spectra recorded on this (2 × 2) structure reveal the opening of a bandgap of about 0.2 eV. A fully (half) hydrogenated germanene surface is obtained after an exposure of about 9000 L hydrogen. The hydrogenated germanene, also referred to as germanane, has a sizeable bandgap of about 0.5 eV and is slightly *n*-type. *Published by AIP Publishing.*

<https://doi.org/10.1063/1.5026745>

The rise of graphene^{1,2} has triggered many scientists to synthesize and study other two-dimensional elemental materials. Silicene, germanene, and stanene, i.e., the silicon, germanium, and tin analogues of graphene, are among these two-dimensional materials that have received quite some attention owing to their similarity with graphene.^{3–7} Theoretical calculations have revealed that silicene, germanene, and stanene exhibit linear dispersing energy bands in the vicinity of *K* and *K'* points of the Brillouin zone.^{8–10} These materials are, just as graphene, semimetals that host massless Dirac fermions. In contrast to graphene, these elemental two-dimensional materials do not occur in nature, and therefore, they have to be synthesized. Another disadvantage of silicene, germanene, and stanene is that they oxidize, i.e., they are not stable at ambient conditions. Despite these disadvantages, there are also several advantages: (1) the honeycomb lattices of silicene, germanene, and stanene are not planar, as in graphene, but buckled, paving the way for the opening of a bandgap by, for instance, applying an external electric field and (2) the spin-orbit coupling in these materials is much larger than that in graphene, making these two-dimensional materials appealing candidates for spintronic-based applications.

Graphene exhibits many interesting and appealing properties, but unfortunately the material cannot be used for field-effect based electronic devices because it is gapless. In principle, a bandgap can be opened in graphene; however, this usually goes at the expense of the high charge carrier mobilities in graphene. Silicene and germanene are, provided that the rather small spin-orbit gap is ignored, also semimetals. Hydrogenated silicene and germanene, usually

referred to as silicane and germanane, respectively, exhibit a sizeable bandgap and still have appreciable charge carrier mobilities.^{11–13}

In 2013, the first successful synthesis of germanane was reported by Bianco *et al.*¹¹ These authors synthesized germanane via the topochemical deintercalation of CaGe₂. Germanane sheets can be obtained by exfoliation since germanane belongs to the family of layered van der Waals materials. At ambient conditions, germanane turns out to be very stable and the material only oxidizes in a time span of several months. This stability is an important prerequisite for the usage of germanane in any technological application. The strong potential of germanane for technological applications is fueled by theoretical calculations, which predict a direct bandgap of 1.5 eV and an electron mobility that is about five times larger than that of bulk germanium.^{12,13} The existence of a bandgap in germanane was confirmed experimentally by Bianco *et al.*¹¹ Inspired by the results of Bianco *et al.*, Madhushankar *et al.*¹⁴ realized a germanane based field-effect transistor. These authors showed that their germanane field effect transistor, which involved a 60 nm thick stack of germanane layers, exhibited ambipolar transport, but the charge carrier mobilities were much lower (~ 70 cm²/V s at room temperature and ~ 150 cm²/V s at 77 K) than the theoretical predicted value (20 000 cm²/V s).

Here, we aim to realize a *single* germanane layer by hydrogenating germanene synthesized in an ultra-high vacuum environment. The germanene sheets are grown on a substrate, and therefore, only one side of the germanene sheet will be exposed to atomic hydrogen. Since only the Ge atoms of the upward buckled hexagonal sub-lattice will be

hydrogenated, the maximum coverage of one monolayer refers to this situation. Our scanning tunneling spectroscopy measurements reveal that full hydrogenation results in the opening of a bandgap of about 0.5 eV. Further exposure to atomic hydrogen leads to roughening of the germanene layer, which we ascribe to intercalation of the atomic hydrogen.

The experiments are performed in an ultra-high vacuum system that is equipped with a room temperature scanning tunneling microscope (Omicron STM1). The base pressure of the ultra-high vacuum system is 3×10^{-11} mbar. The Ge(110) substrates are nearly intrinsic and nominally flat and have dimensions of $10 \times 4 \times 0.5$ mm. The substrates are mounted on a sample holder that only contains molybdenum, tantalum, and aluminum oxide components. After introducing the Ge(110) samples, via a load lock system, into the ultra-high vacuum system, they are carefully degassed at a temperature of 800 K for at least 24 h. Subsequently, the samples are cleaned by several cycles of argon ion bombardment at 500 eV and annealing at 1100 K.¹⁵ Pt is deposited on the Ge(110) substrate by resistively heating a W wire wrapped with high purity Pt(99.995%). After Pt-deposition, the sample is flash annealed at 1100 (± 25) K and subsequently cooled down to room temperature before inserting it into the scanning tunneling microscope for imaging. The aforementioned procedure results in a Ge(110) surface that contains Ge₂Pt clusters with typical dimensions of a few hundreds of nanometers.¹⁶ There are two types of Ge₂Pt clusters: pyramids and flat-topped clusters. The flat-topped clusters exhibit a buckled honeycomb lattice with a lattice constant of 4.2 Å.¹⁶ Scanning tunneling spectroscopy measurements show that the germanene sheet possesses a V-shaped density of states, which is one of the hallmarks of a two-dimensional Dirac material.¹⁷ The steps of the germanene sheets on the Ge₂Pt clusters are quantized in units of 5.6 ± 0.1 Å, i.e., twice the germanene interlayer spacing.¹⁶ The latter suggest that we are dealing with germanene bilayers or multiples thereof, rather than a single germanene layer. This would also explain why the top germanene layer is electronically decoupled from the Ge₂Pt cluster.

The hydrogen adsorption experiments were performed by exposing the sample at room temperature to high-purity molecular hydrogen at a pressure in the range of

1×10^{-7} – 3×10^{-5} mbar. The molecular hydrogen was decomposed into atomic hydrogen using a hot tungsten filament, which was heated to a temperature of about 2000 K. The sample was located in the field of view of the hot tungsten filament at a distance of a few centimeters, which is substantially smaller than the mean free path of the atomic hydrogen.

In Fig. 1(a), a scanning tunneling microscopy image of a flat-topped Ge₂Pt cluster coated with a germanene layer is shown. In the inset, a small scale image of the flat-topped part of the Ge₂Pt cluster is shown. The lattice constant of the hexagonal structure is 4.2 ± 0.1 Å, which agrees well with the findings of Bampoulis *et al.*¹⁶ [see Fig. 1(b)]. Unfortunately, the resolution of this image is insufficient to resolve the downward buckled Ge atoms. The differential conductivity is shown in Fig. 1(c). The observed V-shaped differential conductivity is in good agreement with the results obtained by Zhang *et al.*¹⁷ Upon the exposure of the germanene sheet to 100 L of atomic hydrogen at room temperature, the (1×1) hexagonal structure of germanene changes into a (2×2) hexagonal structure [see Fig. 2(a)]. The (2×2) hexagonal structure still exhibits some defects and adsorbates. The line scan displayed in Fig. 2(b) shows a lattice constant of 0.84 nm, i.e., two times the lattice constant of germanene. The differential conductivity is shown in Fig. 2(c). The hydrogenation results in the opening of a small bandgap of about 0.2 eV. Based on the observed (2×2) structure and the small bandgap opening, we suggest that only half of the upward buckled Ge atoms are hydrogenated, resulting in a hydrogen coverage of 1/2 monolayer (at 1 monolayer coverage, all the Ge atoms of the upward buckled hexagonal sub-lattice of the germanene sheet are hydrogenated). Upon further exposure to atomic hydrogen, the (2×2) structure vanishes and the bandgap opens further. In Fig. 3(b) the differential conductivity of the hydrogenated germanene after an exposure of 9000 L is shown. The bandgap opening amounts about 0.5 eV, and the hydrogenated germanene has become slightly *n*-type. The surface structure exhibits an increase in roughness and disorder, which we ascribe to the intercalation of hydrogen atoms. An scanning tunneling microscopy image is shown in Fig. 3(a). The height variation in this image is about 1 nm. Despite numerous attempts, we were unable to achieve

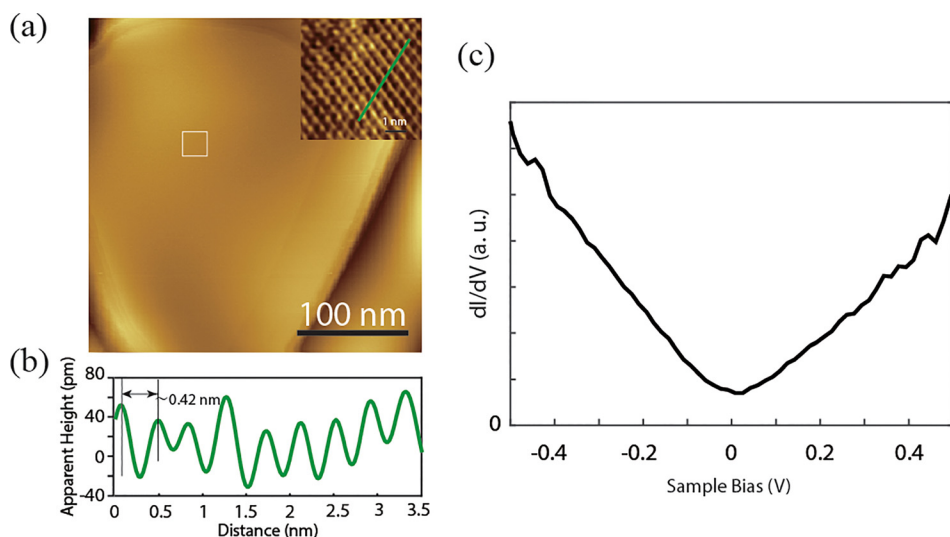


FIG. 1. (a) Scanning tunneling microscopy image of a germanene coated flat-topped Ge₂Pt cluster. Sample bias: -1.5 V and tunneling current: 0.6 nA. Inset: small scale image of the flat-topped part of the germanene coated flat-topped Ge₂Pt cluster. Sample bias: 0.4 V and tunneling current: 0.4 nA. (b) Line profile of the line shown in the inset of graph (a). (c) Differential conductivity (dI/dV) of the germanene coated flat-topped Ge₂Pt cluster. Set points: sample bias -1.5 V and tunneling current 1.0 nA.

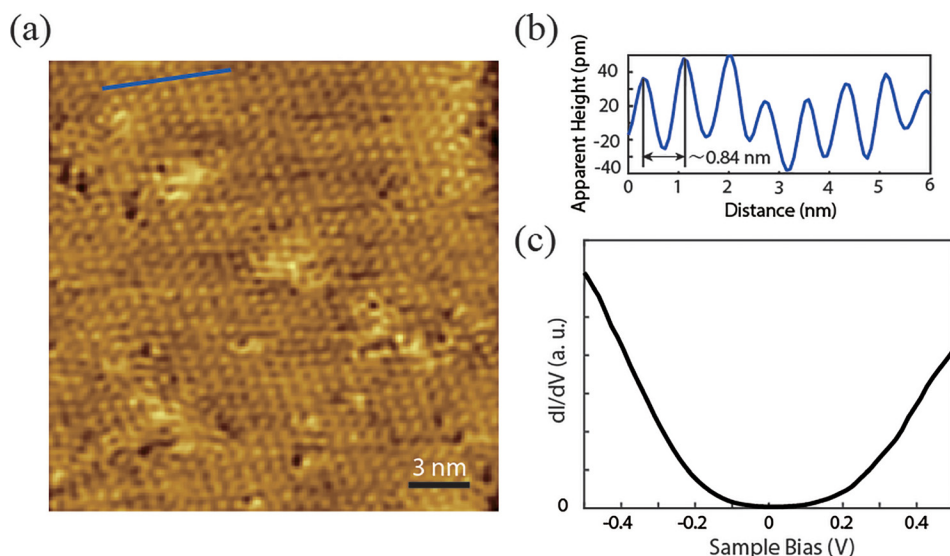


FIG. 2. (a) Scanning tunneling microscopy image of a partly hydrogenated germanene sheet. The lattice constant of the hexagonal structure is 0.84 nm, i.e., twice the value of the pristine germanene sheet. Sample bias: -1.5 V and tunneling current: 1.0 nA. Hydrogen exposure of 100 L. (b) Line profile of the line shown in graph (a). (c) Differential conductivity of the partly hydrogenated germanene. Set points: sample bias -1.0 V and tunneling current 0.9 nA.

atomically resolved scanning tunneling microscopy images, which is probably caused by the increase in roughness and disorder. The exposure to more atomic hydrogen leads to a further increase in the roughness and size of the bandgap. As a final remark, we would like to emphasize that we have not observed any significant spatial variation of the bandgap, indicating that the bandgap cannot be explained by a spatially varying Dirac point.¹⁸

The hydrogenation of germanene and silicene has been studied quite extensively, see Refs. 13 and 18–20 and Refs. 21 and 22 for several theoretical and experimental articles, respectively. Houssa *et al.*¹³ calculated the electronic band structure of germanane using first-principles total energy calculations based on the density functional theory. They found that the bandgap in germanane is direct, independent of the exact atomic configuration, making this material an appealing candidate for optoelectronic applications. Wang *et al.*¹⁹ theoretically studied the properties of half-hydrogenated germanene. These authors found that half-hydrogenated germanene is stable and has a direct bandgap. They also pointed out that the buckling as well as the lattice constant of germanene increases upon hydrogenation. Nijamudheen *et al.*²⁰ demonstrated that the buckling of germanene results in an enhanced chemical reactivity of germanene for hydrogen. To date, there are, unfortunately, no experimental reports on the

hydrogenation of a single sheet of germanene. Luckily, a few experimental studies on the hydrogenation of silicene have been performed recently. The first experimental report on the hydrogenation is by Qiu *et al.*²¹ These authors studied the hydrogenation of a silicene layer synthesized on a Ag(111) substrate using scanning tunneling microscopy and density functional theory calculations. They focused on the (3×3) silicene structure [a (3×3) silicene supercell is commensurate with a (4×4) cell of the Ag(111) surface]. Six out of the 18 Si atoms of a (3×3) silicene unit cell are located on-top, or almost on-top, of a Ag atom and are therefore found in the upward buckled position. The other 12 atoms are found in a downward buckled position. Upon hydrogenation, the regular (3×3) cell, also referred to as the α -(3×3) structure, converts to a γ -(3×3) structure. This γ -(3×3) structure is composed of two distinctly different half unit cells, where one half unit cell has 6 and the other half unit cell has only one upward buckled Si atom.²¹ The hydrogen atoms only adsorb on these upward buckled Si atoms, resulting in a saturation coverage of $7/18$ monolayer. The hydrogen adsorption favors the sp^3 hybridization, leading to an enhancement of the upward buckling and lattice constant. In a second study, Qiu *et al.*²² studied the hydrogenation of the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ silicene phase, which is also commonly found on the Ag(111) surface. In this case, the hydrogen atoms only adsorb on one of the two sublattices of silicene, yielding a perfect half-hydrogenated (1×1) structure.

Based on our experimental results and the available theoretical and experimental data, we arrive at the description of the hydrogenation process of germanene coated Ge_2Pt crystals. At small hydrogen exposures, the hydrogen atoms only occupy the upward buckled Ge atoms. The adsorption of the hydrogen atom on an upward buckled Ge atom leads to an increase in the buckling as well as a small expansion of the surface lattice constant of germanene. The adsorption of hydrogen leads to the development of a compressive surface stress in the germanene sheet. In order to relieve this surface stress, it is energetically favorable to maximize the next-nearest distance of the hydrogenated Ge atoms. At a coverage of $1/2$ monolayer, this results in a (2×2) structure. The next phase of the hydrogenation ($1/2$ to 1 monolayer) process

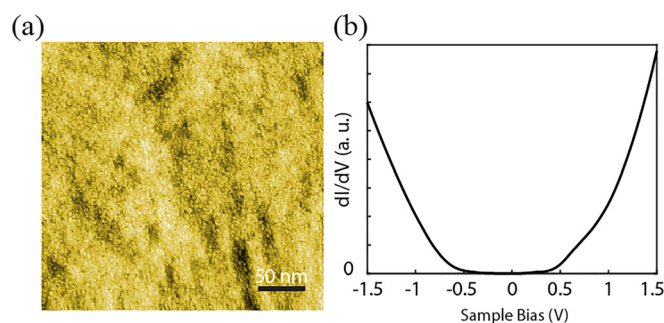


FIG. 3. (a) Scanning tunneling microscopy image of the fully hydrogenated germanene sheet. Image size $300 \text{ nm} \times 300 \text{ nm}$, sample bias -0.8 V, and tunnel current 0.9 nA. (b) Differential conductivity of a fully hydrogenated germanene (1 monolayer of hydrogen). Set points: sample bias -1.5 V and tunneling current 0.9 nA. The hydrogen exposure is 9000 L.

proceeds substantially slower since now also the energetically unfavorable upward buckled Ge atoms need to be hydrogenated. This results in a further increase in the compressive surface stress. Eventually, the germanene sheet becomes fully hydrogenated and exhibits a sizeable bandgap of 0.5 eV. Upon further exposure to hydrogen, we anticipate that hydrogen atoms start to intercalate underneath the half-hydrogenated germanene sheet, leading to an increase in the roughness and a further opening of the bandgap.

We have shown that hydrogenation of germanene, synthesized on Ge₂Pt, results in the opening of a bandgap of about 0.5 eV. At a fractional hydrogen coverage, the (1 × 1) germanene structure converts to a (2 × 2) structure with a bandgap opening of about 0.2 eV. A further increase in the hydrogen exposure leads to vanishing of the (2 × 2) structure and an increase in the bandgap opening to about 0.5 eV. Eventually, the roughness and disorder of the germanene sheet increase, which we ascribe to the intercalation of atomic hydrogen.

Q.Y. acknowledges the China Scholarship Council for financial support. L.Z. acknowledges the MESA+ Institute for Nanotechnology of the University of Twente for financial support. T.A. acknowledges the Ministry of Science, Research, and Technology (MSRT) of Iran for financial support. A.N.R. acknowledges support from the Russian Science Foundation, Grant No. 17-72-20041. H.J.W.Z. acknowledges the Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO) for financial support.

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